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Homo-Diels-Alder reaction of a very inactive diene, bicyclo[2,2,1]hepta-2, 5-diene, with the most active dienophile, 4-phenyl-1,2,4-triazolin-3,5-dione. Solvent, temperature, and high pressure influence on the reaction rate

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Abstract

Solvent, temperature, and high pressure influence on the rate constant of homo-Diels-Alder cycloaddition reactions of the very active hetero-dienophile, 4-phenyl-1,2,4-triazolin-3,5-dione (1), with the very inactive unconjugated diene, bicyclo[2,2,1]hepta-2,5-diene (2), and of 1 with some substituted anthracenes have been studied. The rate constants change amounts to about seven orders of magnitude: from 3.95.10-3 for reaction (1+2) to 12200 L mol-1 s-1 for reaction of 1 with 9,10-dimethylanthracene (4e) in toluene solution at 298 K. A comparison of the reactivity (ln k2) and the heat of reactions (r-nH) of maleic anhydride, tetracyanoethylene and of 1 with several dienes has been performed. The heat of reaction (1+2) is -218 ± 2 kJ mol-1, of 1 with 9,10-dimethylanthracene -117.8 ± 0.7 kJ mol-1, and of 1 with 9,10-dimethoxyanthracene -91.6 ±0.2 kJ mol-1. From these data, it follows that the exothermicity of reaction (1+2) is higher than that with 1,3-butadiene. However, the heat of reaction of 9,10- dimethylanthracene with 1 (-117.8 kJ mol-1) is nearly the same as that found for the reaction with the structural C=C counterpart, N-phenylmaleimide (-117.0 kJ mol-1). Since the energy of the N=N bond is considerably lower (418 kJ/bond) than that of the C=C bond (611 kJ/bond), it was proposed that this difference in the bond energy can generate a lower barrier of activation in the Diels-Alder cycloaddition reaction with 1. Linear correlation (R = 0.94) of the solvent effect on the rate constants of reaction (1+2) and on the heat of solution of 1 has been observed. The ratio of the volume of activation (V≠) and the volume of reaction (V r-n) of the homo-Diels-Alder reaction (1+2) is considered as "normal": V≠/Vr-n = -25.1/-30.95 = 0.81. Copyright © 2012 John Wiley & Sons, Ltd.

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Keywords

4-phenyl-1,2,4- triazolin-3,5-dione, activation volume, bicyclo[2,2,1]hepta-2,5-diene, heat of reaction, homo-Diels-Alder reaction, rate constants, reaction volume